

Theoretical unification between Quenched-Annealed and Equilibrated-Mixture Systems

R. Juárez-Maldonado¹ and M. A. Chávez-Rojó²

¹*Unidad Académica de Física, Universidad Autónoma de Zacatecas. Calzada
Solidaridad esquina con Paseo la Bufa S/N; Zacatecas, Zac. México.*

²*Facultad de Ciencias Químicas, Universidad Autónoma de Chihuahua. Circuito No. 1,
Nuevo Campus Universitario; Chihuahua, Chih. México.*

(Dated: September 1, 2011)

In this paper we apply the self-consistent generalized Langevin equation theory (SCGLE) of dynamic arrest for colloidal mixtures to predict the glass transition of a colloidal fluid permeating a porous matrix of obstacles with random distribution. We obtained the transition diagrams for different size asymmetries and so we give an asserted description of recent simulations results [K. Kim, K. Miyazaki, and S. Saito, *Europhys. Lett.* 88, 36002 (2009)] of Quenched-Annealed and Equilibrated-Mixture systems which reveal very different qualitative scenarios which are in apparent contradiction with theoretical predictions of Mode Coupling Theory (MCT) [V. Krakoviack, *Phys. Rev. E* 75, 031503 (2007)]. We show that SCGLE theory predicts the existence of a reentrant region in EM systems as predicted using MC theory. However, opposite to MCT predictions, we show that it is practically impossible to distinguish a reentrant region in QA systems if it would exist. Qualitative comparisons are in good agreement with simulation results and thus, we propose SCGLE theory as a useful tool for the interpretation of the arrest transition in ideal porous systems.

PACS numbers: 23.23.+x, 56.65.Dy

The study of static and dynamic properties of fluids permeating porous materials is an interesting topic that has attracted increasing attention due to both its relevance in the study of systems in biology, chemistry, physics and engineering [1] and its scientific importance in the understanding of diffusing phenomena [2, 3]. For this, the development of theoretical schemes describing this class of systems has deserved considerable work from many perspectives. In this sense, a binary mixture in which one of the species remains immobile while the second species diffuse constitutes a model system that has been widely employed not only in theoretical or simulation studies [4–9] but also in experimental works [10, 11] as an idealization of a fluid immerse in a porous medium. Despite the simplicity of this model, some parameters like size asymmetry or matrix structure can be selected in order to mimic different systems. There are two protocols widely used to generate the obstacle matrix in order to simulate different classes of disordered porous materials, known as Quenched-Annealed (QA) Mixture and Equilibrated Mixture (EM) [8]. In the first case, the porous matrix is prepared by quenching spherical particles of a monocomponent system in a typical equilibrium configuration and after that, mobile particles are inserted into the void spaces of the matrix of immobilized particles. By the opposite, in the EM protocol, all particles equilibrate together and then, a fraction of them are suddenly immobilized and so, the structure of the obstacle matrix corresponds to that of one species of a mixture in equilibrium.

On the other side, the study of the structural glass transition of fluids is another topic of interest because of its importance in the comprehension of dynamic phe-

nomena as well as for its potential applications in industry. Nevertheless it has attracted a lot of interest in the last decades [12–14], there are still many open problems regarding to the nature of this dynamic phenomenon. For this, it is always desirable to have theoretical schemes that allow for the interpretation of experimental and computer simulation results. In this sense, Mode Coupling Theory (MCT) [14–17] has shown its capability in predicting liquid-glass transitions in a variety of systems and conditions [18–20]. In this context, theoretical studies of liquid-glass transition of fluids confined in porous media deserves special interest in order to achieve a better understanding of the slow dynamics of these systems. Recently, based on the replica Orstein-Zernike equations [4, 21, 22], Vincent Krakoviack has extended the Mode Coupling Theory to consider the glass transition of a fluid immersed in a porous medium [7]. Within this Replica Mode Coupling Theory (RMCT) he obtained the dynamic arrest diagrams for QA mixtures and showed that RMCT predicts a reentry phenomenon for matrix densities higher than the localization threshold. This contribution represents a crucial first step in the theoretical description of the slow dynamics of a fluid immersed in a porous medium.

Because of the complexity of the problem and the variety of scenarios regarding the glass transition in porous media, computer simulation studies have served to reveal some special features that allow to evaluate theoretical predictions. In particular, recent work of K. Kim and coworkers [8] has shown the strong dependence of the glass transition diagram on the protocol in which the porous matrix is prepared. In their work, they performed simulations of hard sphere systems permeating an obsta-

cle matrix prepared using both QA and EM protocols, and compared their results with RMCT predictions. Two important aspects should be addressed: a) by construction, there is no way of predicting EM glass transition diagrams using RMCT and b) simulation results are in apparent contradiction with RMCT prediction about the reentrant behaviour in QA systems.

In this sense, the prediction of dynamic arrest transition diagrams employing an alternative theoretical scheme is crucial for the interpretation of the simulation results mentioned above. The Self Consistent Generalized Langevin Equation theory (SCGLE) has been developed in the context of colloidal systems [23–25] and it has shown their capability in describing the dynamic properties of a variety of systems [26]. The extension of this theory to mixtures has been carried out [27, 28] and allows us to consider QA and EM systems, just assuming that one species does not diffuse. In fact, it has already been employed to describe the time evolution of the collective diffusion properties of a fluid immersed in an ideal porous medium using both protocols [6]. Moreover, there have been derived numerical criteria for the prediction of the liquid-glass transition for several systems and conditions [29–32], requiring as input only structural properties as the static structure factors, $S_{\alpha\beta}(k)$. Actually, it has been shown that, for some cases, this theory is as useful as MCT in the localization of dynamic arrest transitions. Since SCGLE theory has been applied successfully in the description of the dynamics of colloidal fluids permeating ideal porous media as well as in the prediction of the liquid-glass transition in mixtures, it is obvious that the next step in this direction is the extension of this theory to predict the dynamic arrest transitions of QA and EM systems. This is the aim of this work.

The relevant dynamic information of an equilibrium ν -component colloidal suspension is contained in the $\nu \times \nu$ matrix $F(k, t)$ whose elements are the *partial intermediate scattering functions* $F_{\alpha\beta}(k, t) \equiv \langle n_\alpha(\mathbf{k}, t) n_\beta(-\mathbf{k}', 0) \rangle$ where $n_\alpha(\mathbf{k}, t) \equiv \sum_{i=1}^{N_\alpha} \exp[i\mathbf{k} \cdot \mathbf{r}_i(t)] / \sqrt{N_\alpha}$, with $\mathbf{r}_i(t)$ being the position of particle i of species α at time t . The initial value $F_{\alpha\beta}(k, 0)$ is the partial static structure factor $S_{\alpha\beta}(k)$ [33, 34].

The multi-component version of the SCGLE theory consists of a set of exact time-evolution equations that governs the relaxation of the partial intermediate scattering functions $F_{\alpha\beta}(k, t)$ and their self contrapart $F_{\alpha\beta}^{(s)}(k, t) \equiv \delta_{\alpha\beta} \langle \exp[i\mathbf{k} \cdot \Delta\mathbf{R}^{(\alpha)}(t)] \rangle$, where $\Delta\mathbf{R}^{(\alpha)}(t)$ is the displacement of any of the N_α particles of species α over a time t , and $\delta_{\alpha\beta}$ is Kronecker's delta function. The Laplace transform (LT) $F(k, z)$ of the matrix $F(k, t)$, can be written as [27],

$$F(k, z) = \{z + (I + C(k, z))^{-1} k^2 D S^{-1}\}^{-1} S, \quad (1)$$

where the elements of the matrix D are given by $D_{\alpha\beta} \equiv \delta_{\alpha\beta} D_\alpha^0$, with D_α^0 being the diffusion coefficient of species

α in the absence of interactions. This is related with the solvent friction coefficient on an isolated particle of species α , ζ_α^0 , through the Einstein relation, $D_\alpha^0 \equiv k_B T / \zeta_\alpha^0$. The elements $C_{\alpha\beta}(k, z)$ of the matrix $C(z)$ are the LT of the so-called irreducible memory functions $C_{\alpha\beta}(k, t)$ [30]. The corresponding result for the “self” component, $F^{(s)}(k, t)$. Defined as $F_{\alpha\beta}^{(s)}(k, t) \equiv \delta_{\alpha\beta} \langle \exp[i\mathbf{k} \cdot \Delta\mathbf{R}^{(\alpha)}(t)] \rangle$, where $\Delta\mathbf{R}^{(\alpha)}(t)$ is the displacement of any of the N_α particles of species α over a time t , and $\delta_{\alpha\beta}$ is Kronecker's delta, in Laplace space is

$$F^{(s)}(k, z) = \left\{ z + (I + C^{(s)}(k, z))^{-1} k^2 D \right\}^{-1}, \quad (2)$$

where the matrix $C^{(s)}(k, z)$ is the corresponding irreducible memory function which is related with $C(k, z)$ by

$$C(k, z) = C^{(s)}(k, z) = \lambda(k) \Delta\zeta^*(z), \quad (3)$$

The matrix $\Delta\zeta^*(z)$ is a diagonal matrix whose α -th diagonal element, $\Delta\zeta_\alpha^*(z)$, is the Laplace Transform of the time-dependent friction function of particles of species α . Such function reads [31]

$$\Delta\zeta_\alpha^*(t) = \frac{D_\alpha^0}{3(2\pi)^3} \int d^3k k^2 [F^{(s)}(k, t)]_{\alpha\alpha} [c\sqrt{n}F(k, t)S^{-1}\sqrt{n}h]_{\alpha\alpha}, \quad (4)$$

with the elements of the k -dependent matrices h and c being the Fourier transforms $h_{\alpha\beta}(k)$ and $c_{\alpha\beta}(k)$ of the Ornstein-Zernike total and direct correlation functions, respectively. Thus, h and c are related to S by $S = I + \sqrt{n}h\sqrt{n} = [I - \sqrt{n}c\sqrt{n}]^{-1}$, with the matrix \sqrt{n} defined as $[\sqrt{n}]_{\alpha\beta} \equiv \delta_{\alpha\beta}\sqrt{n_\alpha}$.

As illustrated in Ref. [31], the solution of the SCGLE theory provides the time and wave-vector dependence of the dynamic properties of the system contained in $F(k, t)$ and $F^{(s)}(k, t)$. It also provides equations for their long-time asymptotic values, referred to as non-ergodicity parameters, which play the role of order parameters for the ergodic–non-ergodic transitions. The most fundamental of these results [31] is the equation for the asymptotic mean squared displacement $\gamma_\alpha \equiv \lim_{t \rightarrow \infty} \langle (\Delta\mathbf{R}^{(\alpha)})^2 \rangle$, which reads,

$$\frac{1}{\gamma_\alpha} = \frac{1}{3(2\pi)^3} \int d^3k k^2 \{ \lambda[\lambda + k^2\gamma]^{-1} \}_{\alpha\alpha} \times \{ c\sqrt{n}S\lambda[S\lambda + k^2\gamma]^{-1}\sqrt{n}h \}_{\alpha\alpha} \quad (5)$$

where S is the matrix of partial static structure factors, h and c are the Ornstein-Zernike matrices of total and direct correlation functions, respectively, related to S by $S = I + \sqrt{n}h\sqrt{n} = [I - \sqrt{n}c\sqrt{n}]^{-1}$, with the matrix \sqrt{n} defined as $[\sqrt{n}]_{\alpha\beta} \equiv \delta_{\alpha\beta}\sqrt{n_\alpha}$, and $\lambda(k)$ is a diagonal

matrix given by $\lambda_{\alpha\beta}(k) = \delta_{\alpha\beta}[1 + (k/k_c^{(\alpha)})^2]^{-1}$, where $k_c^{(\alpha)}$ is the location of the first minimum following the main peak of $S_{\alpha\alpha}(k)$.

To generalize the SCGLE theory to calculate the dynamic properties $F_{\alpha\beta}(k, t)$ of a colloidal fluid mixture of μ components immersed in a porous matrix, we use the same model employed in Ref. [6]. This consists of a ν -component colloidal mixture where a fraction of the particles, μ of the ν species, are diffusing in the random matrix of obstacles formed by restant $\nu - \mu$ immobile (self-diffusion coefficients identically zero) species which play the roll of porous medium. The derivation of corresponding equations to calculate the partial intermediate scattering functions $F(k, t)$, $F^{(s)}(k, t)$ and the long time mean squared displacement $\gamma_\alpha \equiv \lim_{t \rightarrow \infty} \langle (\Delta \mathbf{R}^{(\alpha)})^2 \rangle$ of the mobile species is immediate. Simply we make the self-diffusion coefficients $D_\alpha^0 = 0$ of all species that represents the immobile particles in the system of Eqs. 1, 2 and 4, the result is a reduced set of μ equations for the μ mobile species, with the same functional form.

We will consider a binary hard sphere mixture of N_1 mobile particles of diameter σ_1 and N_2 obstacle particles of diameter σ_2 . The only macroscopic control parameters are the volume fractions $\phi_i = \pi n_i \sigma_i^3 / 6$, where $n_i = N_i / N$ and $N = N_1 + N_2$, and the size asymmetry defined as $\delta = \sigma_1 / \sigma_2$. The information about the mobility of the particles is contained in the self diffusion coefficients, D_α^0 , so that, making $D_2^0 = 0$ in Eq. 4 implies that particles of species 2 remain immobile. On the other hand, the structure of the porous medium is contained in the matrix of static structure factors, S . In practice, the selection of the protocol to generate the porous matrix determines the way on calculating the elements of matrix S . In this work, we used replica Ornstein-Zernike equations with given as the input to obtain the rest of the elements of the matrix S . Thus, for $S_{22}(k)$ we employed the static structure factor of a monodisperse system in the case of QA mixtures, and a static structure factor of a binary mixture in the case of EM systems.

In Fig. 1 we compare the dynamic arrest diagrams obtained using Eq. 6 with both protocols to explore the sensitivity of our theory to the morphology of the medium. Dashed lines correspond to Quenched-Annealed (QA) and solid lines correspond to Equilibrated-Mixture (EM). Three size asymmetries were studied: $\delta = 0.5, 1$ and 2 ; upper (black), middle (red) and lower (green) curves respectively. Observe that EM protocol shows an evident reentrance while for QA mixtures it is practically impossible to distinguish the existence of a reentrant region. We argue that this difference arises from the fact that thermalization process in EM systems, in which both species equilibrate together, leads to a self-generation of free-volume by mobile particles. This is easy to understand considering the fact that an increase in the number of fluid particles for a fixed number of obstacles implies

an increase in the total density which means less volume occupied by particle and so, in certain region of the transition diagram, once the obstacle particles are quenched, the fluid has more free volume available to diffuse. On the other hand, in QA systems, the volume occupied by the obstacles is the same independent of the concentration of fluid particles. So, an increase on the number of fluid particles would not increase their mobility, in principle, and for that reason there is not a reentrant region for QA systems. These predictions are in agreement with computer simulation results reported in Ref. [8, 6].

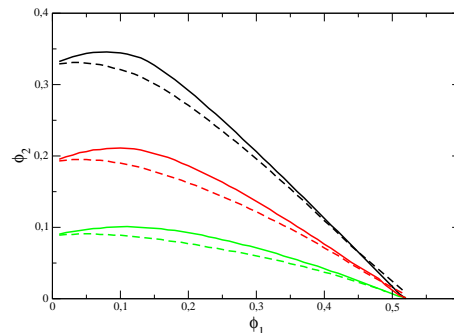


FIG. 1: Dynamic arrest phase diagrams of a monodisperse Hard Sphere fluid immersed in a random porous medium prepared in two different models: Quenched-Annealed (dashed lines) and Equilibrated-Mixture (continuous lines). And three size asymmetries ratios between fluid and matrix particles: bottom $\delta = 0.5$ (black), intermediate $\delta = 1$ (red) and top $\delta = 2$ (green). (Color on line)

Qualitative comparisons between SCGLE predictions and computer simulation results are shown in figure 2 where we plot the SCGLE transition line (continuous line) and the fluid (solid) and arrested (open) states determined by computer simulation experiments of Kim et. al. for QA mixtures (upper panel) and EM systems (lower panel). Vertical axis corresponds to the obstacle volume fraction scaled with the percolation volume fraction, ϕ_p , and horizontal axis corresponds to the mobile particles volume fraction scaled with the monocomponent glass transition volume fraction, ϕ_p . For reference, we also plotted (dash line) the arrest transition line predicted by Krakoviack with RMCT for QA systems. It deviates considerably from simulation results and predicts a reentrancy that cannot be appreciated in simulation experiments. He explained this reentrancy in terms of the delocalization of mobile particles caused by occasional collisions with other fluid particles trapped in neighbor cages. We believe that this effect -if there exist- could not be responsible of the reentrant pocket, as it has been pointed out in Ref. [8] where the authors have shown that it is hard to identify the existence of a reentrant region in the arrest transition diagram obtained with molecular simulations.

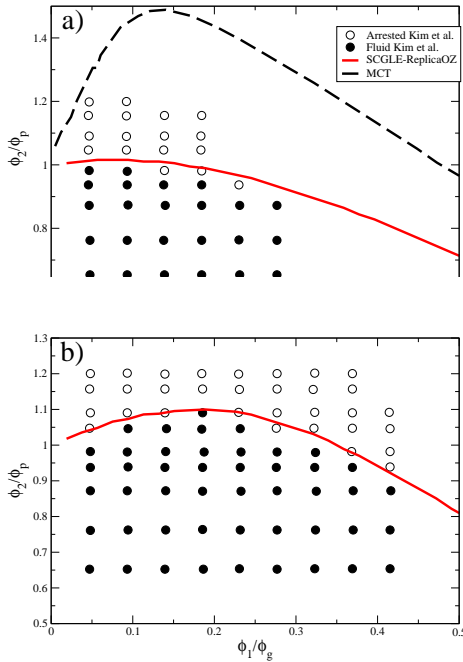


FIG. 2: Qualitative comparison between dynamic arrest diagram of hard sphere fluid absorbed in a random porous medium calculated with SCGLE theory (continuous line) and simulations of Kim et al (fill symbols fluid phase and empty symbols arrested phase), for both QA (upper panel) and EM (lower panel) systems. RMCT prediction (dash line) is shown by reference.

To understand the reentrant behavior of arrest transition diagrams with both protocols, one must carefully analyze the mechanisms that give rise to this phenomenon in both EM and QA systems. First, Krakoviack proposed a mechanism to explain the notorious reentrancy in the diagram predicted by RMCT with QA protocol [7], arguing that the dephasing of trajectories of the caged mobile particles by collision with other mobile particles causes an increase in the percolation threshold. Although this mechanism could explain the existence of a reentrancy, says nothing about the magnitude of this effect. We think, in agreement with arguments of Kim et. al. [8], that even when those collisions can eventually occur, the structure of the porous matrix is not modified and consequently the effects on the phase diagram should not be very noticeable. Thus, if this reentrant region does exist in the arrest diagram, the mesh size of the simulation should be finer to show it clearly. This fact could be observed in Fig. 2 where the transition line predicted using SCGLE theory shows a barely noticeable reentrance. On the other hand, in the case of the EM protocol, the reentrancy is well understood and has already been explained in Ref. [8]. The fact that both species (mobile and immobile) are equilibrated together before stopping the obstacle particles, implies that increasing the concen-

tration of mobile particles, due to purely entropic effects, they generate their own space to continue moving. For that, unlike the case of QA, in EM systems the structure of the porous matrix is affected by this increase and so, the reentrance is highly visible, as shown by MD results and theoretical (SCGLE) curve.

In summary, we have applied SCGLE to predict the dynamic arrest transition in a fluid permeating a porous matrix using Quenched-Annealed and Equilibrated Mixture protocols to generate the obstacle positions. As it has been shown in previous works, this theoretical scheme leads to an accurate description of the slow dynamics phenomena of fluids under different conditions. As can be seen in this work, SCGLE approach is capable to predict the arrest transition diagrams in this kind of systems, independently of the protocol followed to generate obstacle positions. The required input are the static structure factors of the mixture which could be calculated using ROZ equations with an appropriate closure relation, once the protocol is defined. For EM systems, SCGLE arrest transition line is in excellent qualitative agreement with computer simulation results, showing a notorious reentrant pocket which is well understood and has already been discussed in this work and in Ref. [[8]]. On the other hand, for QA mixtures, we could compare our predictions with both computer simulations and another theoretical approach, Replica Mode Coupling Theory. The qualitative agreement with computer simulation results is as good as in EM systems, but unlike RMCT predictions, the reentrant pocket is barely noticeable. In this way, we think that SCGLE has provided us with a theoretical approach to predict dynamic arrest in mobile-immobile mixtures independently of the structure of the obstacle matrix in a unified way, just providing the appropriate static inputs.

This work was supported by Consejo Nacional de Ciencia y Tecnología through grants CB-2010-C01-156423 and Red Nacional de Nanociencias y Nanotecnología.

-
- [1] M. Sahimi, Rev. Mod. Phys. 65, 1393 (1993).
 - [2] R. Evans, J. Phys.: Condens. Matter 2, 8989 (1990).
 - [3] G. B. McKenna, Eur. Phys. J. Special Topics 141, 291 (2007).
 - [4] W. G. Madden y E. D. Glandt, J. Stat. Phys. 51, 537 (1988).
 - [5] G. Viramontes Gamboa, J. L. Arauz Lara y M. Medina Noyola, Phys. Rev. Lett. 75, 759 (1995).
 - [6] M. A. Cavez Rojo, R. Jarez Maldonado y M. Medina Noyola, Phys. Rev. E 77, 040401(R) (2008).
 - [7] V. Krakoviack. Phys. Rev. Lett. 94, 065703 (2005). V. Krakoviack. Phys. Rev. E 75, 031503 (2007).
 - [8] K. Kim, K. Miyazaki, and S. Saito, Europhys. Lett. 88, 36002 (2009). K. Kim, K. Miyazaki and S. Saito, Eur. Phys. J. Spec. Top. 189, 135 (2010). K. Kim, K. Miyazaki, and S. Saito, J. Phys.: Condens. Matter 23,

- 234123 (2011).
- [9] J. Kurzidim, D. Coslovich and G. Kahl, Phys. Rev. Lett. 103, 138303 (2009). J. Kurzidim, D. Coslovich and G. Kahl, Phys. Rev. E 82, (2010). J. Kurzidim, D. Coslovich and G. Kahl, J. Phys.: Condens. Matter 23, 234122 (2011).
 - [10] G. Cruz de León, J. M. Saucedo Solorio and J. L. Arauz Lara, Phys. Rev. Lett. 81, 1122 (1998). G. Cruz de León and J. L. Arauz-Lara, Phys. Rev. E, 59, 4203 (1999).
 - [11] S. G. J. M. Kluijtmans, G. H. Koenderink and A. P. Philipse, Phys. Rev. E 61, 626 (2000).
 - [12] C. A. Angell, Science 267, 1924 (1995).
 - [13] P. G. Debenedetti and F. H. Stillinger, Nature 410, 359 (2001).
 - [14] W. Götze in Liquids, Freezing and Glass Transition, edited by J. P. Hansen, D. Levesque, and J. Zinn-Justin (North-Holland, Amsterdam, 1991).
 - [15] G. Nägele and J. K. G. Dhont, J. Chem. Phys. 108, 9566 (1998).
 - [16] A. J. Banchio, J. Bergholtz, and G. Nägele, J. Chem. Phys. 113, 3381 (2000).
 - [17] G. Nägele, J. Bergholtz and J. K.G. Dhont, J. Chem. Phys. 110, 7037 (1999).
 - [18] K. N. Pham et al., Science 296, 104 (2002).
 - [19] G. Szamel, Phys. Rev. Lett. 90, 228301 (2003).
 - [20] F. Sciortino and P. Tartaglia, Adv. Phys. 54, 471 (2005).
 - [21] W. G. Madden, J. Chem. Phys. 96, 5422 (1992).
 - [22] J. A. Given and G. Stell, J. Chem. Phys. 97, 4573 (1992).
 - [23] L. Yeomans-Reyna and M. Medina-Noyola, Phys. Rev. E. 62, 3382 (2000).
 - [24] L. Yeomans-Reyna and M. Medina-Noyola, Phys. Rev. E. 64, 066114 (2001).
 - [25] R. Juárez-Maldonado, M. A. Chávez-Rojó, P. E. Ramírez-González, L. Yeomans-Reyna, and M. Medina-Noyola, Phys. Rev. E 76, 062502 (2007).
 - [26] L. Yeomans-Reyna, H. Acua-Campa, F. Guevara-Rodríguez and M. Medina-Noyola, Phys. Rev. E 67, 021108 (2003).
 - [27] M. A. Chávez-Rojó and M. Medina-Noyola, Physica A 366, 55 (2006).
 - [28] M. A. Chávez-Rojó and M. Medina-Noyola, Phys. Rev. E 72, 031107 (2005).
 - [29] P.E. Ramírez-González *et al.*, Rev. Mex. Física 53, 327 (2007).
 - [30] L. Yeomans-Reyna, M. A. Chávez-Rojó, P. E. Ramírez-González, R. Juárez-Maldonado, M. Chávez-Páez, and M. Medina-Noyola, Phys. Rev. E 76, 041504 (2007).
 - [31] R. Juárez-Maldonado and M. Medina-Noyola, Phys. Rev. E 77, 051503 (2008).
 - [32] R. Juárez-Maldonado and M. Medina-Noyola, Phys. Rev. Lett. 101, 267801 (2008).
 - [33] J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids* (Academic Press Inc., 1976).
 - [34] G. Nägele, Phys. Rep. **272**, 215 (1996).